Electrochemical Application of Carbon -Coated Inorganic Materials with Uniform Pores

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論文内容要旨

Chapter 1: Introduction

Since the later half of 1990's, a new class of porous carbons with uniform pore structures have been developed.[1,2] They can be prepared by using template substances such as inorganic crystals or thermoplastic polymers and are called ordered porous carbons. Though the ordered porous carbons are expected to be used as effective sorbents, catalyst supports, and electrodes, their structure variety, pore controllability, and structure regularity are still not sufficient compared with inorganic porous materials such as anodic aluminum oxide (AAO) films and mesoporous silicas. In this study, we focus on "carbon-coated inorganic materials with uniform pores".[3,4] The coated materials retain their inherent highly uniform pore structures, and in addition, their pore surfaces have carbon nature, i.e., hydrophobicity, chemical stability, and electrical conductivity unlike the present inorganic materials. There are, however, quite few reports on the application of such coated materials to electrochemistry. The purpose of this work is to demonstrate the ability of the carbon-coated inorganic materials in the electrochemical field, and to open up the way to prepare a new class of porous electrodes which have different properties from the conventional ordered mesoporous carbons.

Chapter 2: Enhancement Mechanism of Electrochemical Capacitance in Nitrogen-/Boron-Doped Carbons with Uniform Straight Nanochannels

We first demonstrate that the carbon-coated inorganic material is very useful for fundamental research in the electrochemistry.[5] Electric double layer capacitor is an electrical storage device that can be repeatedly charged and discharged like secondary batteries. Though it is generally recognized that its capacitance can be increased by the doping of heteroatoms, such as nitrogen and boron, into a porous carbon electrode, the enhancement mechanism is not fully understood, due to the differences of pore structures between the doped and undoped carbon electrodes. In this chapter, AAO with uniform straight nanochannels was completely coated with pure, N-doped or B-doped carbon layers, and their electric double layer capacitances are measured in an aqueous (1 M sulfuric acid, Figure 1) and organic (1 M

Et_4NBF_4/polypropylene carbonate) electrolyte solutions in order to investigate the capacitance enhancement mechanisms caused by N- or B-doping. Since the three types of carbon-coated AAOs (pure, N-doped or B-doped) have exactly the same pore structure, the observed capacitance enhancement was ascribable to only the following factors; (i) better wettability, (ii) the decrease of equivalent series resistance, (iii) the contribution of space-charge-layer capacitance, and (iv) the occurrence of pseudocapacitance. From the measurements of the wettability and the electrical resistance of the coated AAOs together with the electrochemical investigation (the cyclic voltammetry, the galvanostatic charge/discharge cycling and the impedance analysis), it is concluded that the pseudocapacitance through faradic charge transfer (factor iv) is the most important factor to enhance the capacitance by N- or B-doping. This can be applied to not only the present carbon-coated AAOs but also any other porous carbons.

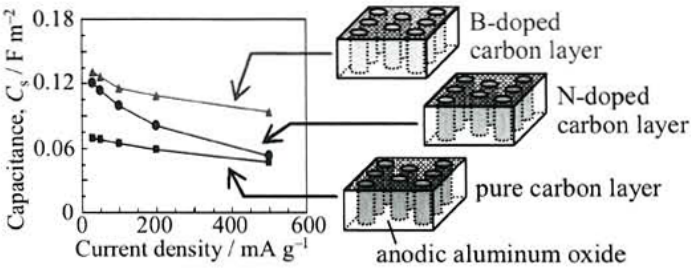

Figure 1 Capacitance per surface area of the coated AAOs with pure, N-doped or B-doped carbon layers in 1M H_2SO_4 as a function of the current density. N- or B-doped samples exhibit higher capacitances than undoped one, especially at low current density.

Chapter 3: Carbon-Coated Mesoporous Silicas as Electrode Materials

We showed that the carbon-coated AAO is a very nice model porous material in Chapter 2. However, the coated AAO is not practical as an electrode material due to its limited specific surface area as small as 30 m^2 g^{-1}. We then examine the possibility of the carbon-coated mesoporous silicas which have enough high surface area up to 530 m^2 g^{-1} as electrode materials in Chapter 3.[6] The entire pore surface of FSM-16 type mesoporous silica was uniformly coated with thin carbon layer by carbonizing pre-doped organic-alcohol molecules onto the pore surface. The thickness of the carbon layer was estimated to be extremely thin, i.e., it corresponds to only 1~2 graphene layers. Even after the carbon-coating, FSM-16 preserves its intrinsic ordered pore structure (hexagonal array of cylindrical pores) and still possesses high surface area of 530 m^2 g^{-1}, but its pore nature is completely changed into hydrophobic one, which was revealed from little amount of water-vapor adsorption. We characterized electrochemical properties of the carbon-coated FSM-16 together with the carbon-coated SBA-15 synthesized by using the same coating method. Both of them exhibit electric double-layer capacitance in 1 M H_2SO_4 (Figure 2) and 1 M NaCl and the values are comparable to those of the conventional activated carbons. We can thus conclude that the

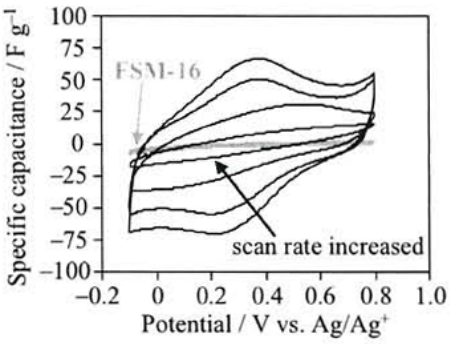

Figure 2 Cyclic voltammograms of carbon-coated FSM-16 in 1 M H_2SO_4. Scan rates were 0.5, 1, 10, and 50 mV s^{-1}. For comparison, a cyclic voltammogram of FSM-16 (at 0.5 mV s^{-1}) is also presented as a gray line.

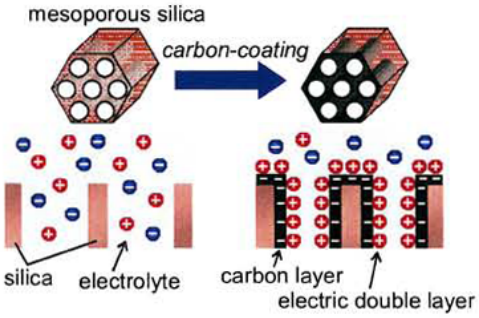

Figure 3 An image of the change of the surface property by the carbon-coating.

present carbon coating changes the nature of mesoporous silica from an insulator to an electrical conductor with its ordered pore structure unchanged (Figure 3), and the carbon-coated mesoporous silicas can be used as electrode materials.

Chapter 4: Carbon-Coated Mesoporous Silica Film with Large Continuous Face for Effective Electrode

The conventional porous carbons including the ordered mesoporous carbons are generally synthesized as powders. Accordingly, they are usually mixed with binder polymers to form uniform sheets, and then used as electrodes. The electrode sheets thus prepared inevitably contain random macropores in the interparticle spaces, i.e., it is impossible to prepare the porous electrodes which contain only uniform-sized mesopores. In addition, such electrode sheets have noticeable interparticle electrical-resistance which increases the inner resistance. To overcome these problems, we conduct a uniformly carbon-coating on a continuous mesoporous silica film (MSF) with 3D accessible pores[8] to obtain a porous electrode which is free from random macropores and interparticle resistance in Chapter 4.[7] By the carbon coating, surface of MSF became hydrophobic as is found by Figure 4. In addition, we confirmed that C/MSF retains the ordered mesoporous structure even after a high heat-treatment temperature of 1073 K (Figure 5). We found that the carbon isolated from C/MSF by HF washing has uniform-sized mesopores from the high-resolution TEM observation, and this fact indicates that carbon layer continuously covers the mesopores of MSF. Interestingly, the cyclic voltammogram of C/MSF in 1M H_2SO_4 keeps almost the same pattern even under larger scan rates up to 200 mV s^{-1} (Figure 6). This excellent rate performance can be ascribed to the film shape (free from interperticle resistance) and to the small ion-transfer resistance in the 3D accessible ordered mesopores.

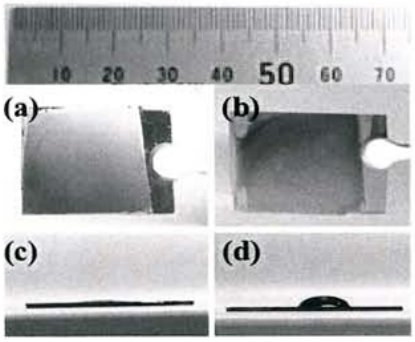

Figure 4 Photographs of (a) MFS and (b) C/MSF formed on a substrate, and (c,d) their images with a water droplet.

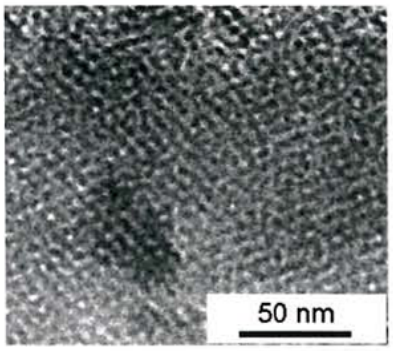

Figure 5 TEM image of C/MSF.

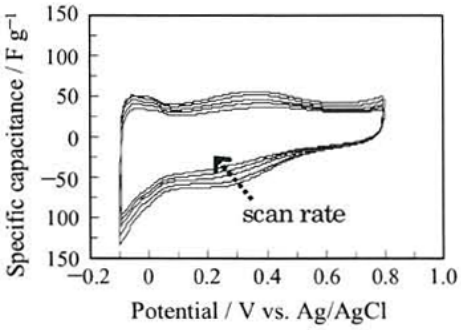

Figure 6 Cyclic voltammograms of C/MSF in 1 M H_2SO_4. Scan rates are 10, 20, 50, 100 and 200 mV s^{-1}.

Chapter 5: Conclusions

We examined the possibility of the carbon-coated inorganic materials with uniform pores in the electrochemical field. In Chapter 2, we demonstrated that the coated material has better pore controllability than the conventional ordered porous carbons, and therefore, the coated material is significantly useful for the fundamental research in the electrochemistry as a model porous material. In Chapter 3, we proved that the carbon-coating approach can be applied even to mesoporous silicas with small pore diameters of 3 to 7 nm, and the entire silica surface has become electrically conductive one. Furthermore, we succeeded in the preparation of a porous electrode film which is free from random macropores and interparticle

resistance by the carbon-coating of a mesoporous silica film with a large continuous face (Chapter 4). It has been thus revealed that the carbon-coated inorganic materials are extremely useful in the electrochemical field, and consequently they are expected to be further developed as model porous materials or effective electrode materials of batteries or biosensors.

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論文審査結果の要旨

活性炭を代表とする多孔質炭素の高性能化のためには細孔構造のナノレベルでの制御が必須である。そのような構造制御法として鋳型法が提案されているが、鋳型と同じ構造が得られない、鋳型除去のためにフッ酸処理が必要、構造規則性が低いなどの欠点がある。本研究では、均一で規則的な細孔をもつ無機物質の全表面を炭素で完全に被覆した材料を合成することで従来法の欠点を克服し、さらに絶縁体である無機多孔体であっても炭素被覆さえすれば電気化学分野に応用できることを実証している。本論文はこれらの結果をまとめ、炭素被覆無機多孔体の電極材料としての有効性を示したもので全編５章よりなる。

第１章は緒論であり、本研究の背景、従来の知見、目的および意義について述べている。

第２章では、細孔構造が制御された炭素被覆無機多孔体をモデル物質として利用することで、N 原子および B 原子ドープによる電気二重層容量増加の機構を解明している。直線状細孔をもつアルミニウム陽極酸化皮膜に N 原子あるいは B 原子をドープした炭素を被覆することで、細孔構造は全く同じであるがドープされた原子だけが異なる試料を作製した。これらの試料の電気二重層容量を様々な条件で測定することで、ドーピングによる電気二重層容量増加は炭素表面と電解質の間の電子の授受による疑似容量の発現によるものであることを明らかにしている。

第３章では、規則的な直線状メソ細孔をもつメソポーラスシリカの全細孔表面を炭素で均一に被覆し、電極材料として評価している。メソポーラスシリカとして細孔径 7.0 nm の SBA-15 と細孔径 3.3 nm の FSM-16 に炭素被覆を試みたところ、細孔径が小さい FSM-16 であっても、表面シラノール基の量さえ十分であれば炭素の均一な被覆が可能であることを明らかにしている。さらにどちらの炭素被覆メソポーラスシリカとも活性炭とほぼ同様の電気二重層容量が発現し、炭素被覆することでメソポーラスシリカの全細孔表面に導電性が付与されたことを実証している。

第４章では、白金を被覆したシリコン基板上に炭素被覆メソポーラスシリカ膜を作製し、電極としての性能を評価している。作製したメソポーラスシリカ膜のサイズは 2 x 2 cm と非常に大きいが、均一に炭素被覆できることを明らかにしている。さらに炭素被覆メソポーラスシリカ膜は、バインダーや導電助剤が不要で、内部抵抗も極めて低く、水溶液中でも安定で、ポルフィリンのような大分子でも固定化し電荷移動を起こすことが可能である非常に優れた電極であることを実証している。

第５章は結論であり、研究全体の総括を行っている。

以上、ようするに本論文は、炭素被覆した均一多孔性無機物質は電気化学においてモデル物質として極めて有用であるばかりでなく、高性能な電極材料としても非常に有望であることを明確に示したもので、材料化学の発展に寄与するところが多い。

よって、本論文は博士(工学)の学位論文として合格と認める。